

Direct Methanol Fuel Cells

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Objectives

Develop materials and components and optimize operating conditions of the direct methanol fuel cell (DMFC) for maximum power density and fuel conversion efficiency at a minimum cost. In particular:

- Design and optimize membrane-electrode assemblies (MEAs) to enhance cell performance.
- Advance electrocatalysis of methanol oxidation and oxygen reduction to increase power density and lower total precious metal loading.
- Characterize and optimize non-Nafion polymers with reduced crossover and improved performance.
- Model, develop and demonstrate practical viability of advanced cell components.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- D. Fuel Cell Power System Benchmarking
- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Build, operate and test performance of DMFCs with different anode and cathode catalysts, membranes and MEAs.
- Through experimentation, develop thorough understanding of the key factors impacting cell performance and durability.
- Maximize efficiency, power and energy density of DMFCs by creative designing of stack components and experimental verification of the hardware performance.

Accomplishments

Cathode Research

- Carbon-supported Pt catalysts optimized for performance at a loading of 0.6 mg cm⁻².
- Respectable performance demonstrated at an air stoichiometric ratio between 2 and 3.

Electrocatalysis

- Alternative carbon-supported cathode catalyst demonstrated for over 200 hours with power density ~15% better than that of a reference Pt catalyst.
- Key factors affecting the performance of Pt-Ru anode catalysts determined by a combination of electrochemical ("in fuel cell"), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and CO-stripping techniques.

Performance Durability

- Effect of Pt oxide formation on short-term DMFC performance determined; a method of regaining cathode activity developed and successfully implemented in life testing.
- Ruthenium crossover through Nafion[®] membrane and its effect on the cathode activity demonstrated for the first time; other reasons for long-term MEA degradation identified.

Membrane Research

- Significant selectivity improvement over non-fluorinated bi-phenol sulfone (BPSH) polymers achieved with two fluorinated poly(arylene ether sulfone) polymers: 6F [hexafluorinated (biphenol A) sulfonated poly(arylene ether sulfone)] and 6F-CN [hexafluorinated / nitrile-functional sulfonated poly(arylene ether sulfone)].
- Low-resistance 6F-CN MEAs prepared and successfully tested in a DMFC for several hundred hours with tolerable performance degradation.

Stack R&D

- Three generations of 11-W stacks for a 20-W DMFC system for portable power designed, built and tested.
- Four latest-generation stacks delivered to Ball Aerospace for system integration.
- Design of all components for the 500-W auxiliary power unit (APU) DMFC stack completed; excellent performance demonstrated with a six-cell short stack operating at zero cathode backpressure and air stoichiometry ratio below three.

Future Directions

- Investigate the mechanism and design methods for controlling degradation of the Nafion[®] and non-Nafion MEAs.
 - Optimize performance and improve durability of systems based on novel alternative membranes, such as 6F and 6F-CN.
 - Perform theoretical and practical study of the impact of catalyst layer structure on the rate of methanol oxidation and oxygen reduction.
 - Investigate novel carbon-supported catalysts for low-loading DMFC operation.
 - Improve DMFC performance by understanding and optimizing hydrophilic/hydrophobic properties of the cathode.
 - Demonstrate for at least 100 hours sustained operation of a large-surface area stack with air stoichiometry ratio below two.
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Introduction

Direct methanol fuel cell research at Los Alamos National Laboratory (LANL) has focused on developing materials and designing optimum operating conditions for DMFCs to be used in portable power applications (commercial electronics, battery replacement for the military) and transportation (on-board APUs). The main objective of LANL's research effort in the DMFC area has been to demonstrate that methanol-based systems can meet power-density, energy-conversion efficiency and cost targets.

Results

In our FY 2003 research, we continued our effort to optimize carbon-supported catalysts for the main purpose of reducing the precious metal loading in DMFCs. Five cathode Pt/C catalysts with Pt content ranging from 30 wt% to 80 wt% were tested at a target catalyst loading of $0.6 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. Experiments revealed that 56% Pt/C and 60% Pt/C are not only the most active for oxygen reduction, but are also more immune to methanol crossover effects. DMFC performance recorded with the 80% Pt/C was not as good as that of 56% Pt/C and 60% Pt/C, yet was much above that of the 40% Pt/C and 30% Pt/C.

Last year, we introduced a new binary cathode catalyst, Pt-X/C (patent application pending), with higher activity towards oxygen and improved methanol tolerance compared to the Pt/C reference catalyst. In FY 2003, we demonstrated superior performance of that catalyst in a 200-hour life test. The Pt-X performance at the end of the life test, 15% better than that of a reference Pt/C catalyst, would have been even better had it not been for its relatively poor long-term stability. Future research will focus on improving the stability of this catalyst, which could lead to as much as 50% improvement in the cell performance. An attempt will also be made to obtain the Pt-X catalyst in an unsupported form, more suitable for portable DMFC use.

Progress in cathode and cell-component research has led to significant lowering of the airflow required to maintain good cell performance. In FY 2003, we demonstrated single cells and prototype stacks that, in addition to showing good performance and high efficiency, can operate on ambient air and with an air

stoichiometry ratio of ~ 2.3 . This low stoichiometry exceeds the airflow reduction milestone of the DMFC project at LANL.

The current year marks a very significant increase in the DMFC durability research at LANL. We developed a setup for the parallel durability testing of several MEAs as well as techniques for detecting performance losses of different MEA components. We have extensively used carbon monoxide probing for determining the number of active catalyst sites and atomic composition of the anode and cathode surfaces at various times of the life test. All durability research was carried out under practical cell operating conditions, at low flow and pressure of the cathode air and high cell operating voltage. As indicated by the life-test data in Figure 1, most of the short-term DMFC performance losses occur in the first 24 hours of the life test. This loss has been attributed to the surface oxidation of the platinum catalyst at its operating potential of 0.80-0.85 V. It can be regained by reducing the catalyst surface, for example, by stopping the cathode airflow for a few seconds (Figure 2).

In addition to short-term performance loss caused by oxidation of the Pt surface, DMFCs also suffer from long-term (generally irreversible) performance degradation. This performance loss is most likely due to changes in the hydrophobic/hydrophilic properties of the cathode, loss of the

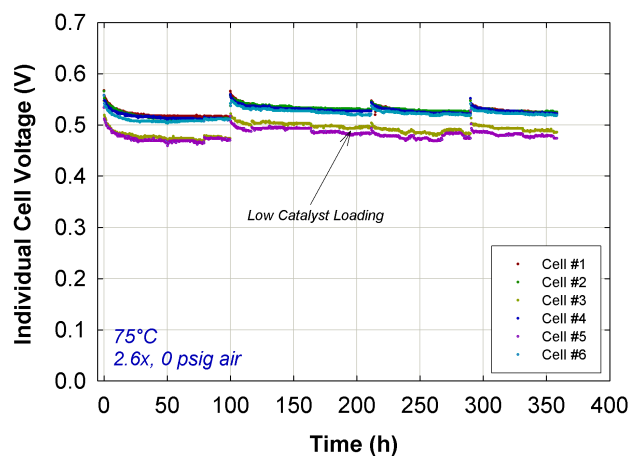


Figure 1. A 350-hour Parallel Life Test of Six Cells Operated at a Constant Current Density of 0.08 A cm^{-2} at 75°C

ionomer from the electrodes (cathode in particular), and lowering of the cathode activity as a result of ruthenium crossover and its re-deposition at the Pt surface. Ruthenium crossover was first demonstrated at LANL in FY 2003 by using the carbon monoxide probe technique. This research will continue in FY 2004, focusing on the methods of stabilizing Ru in the DMFC anode.

In the past year, we developed alternatives to standard Nafion[®] MEAs that for the first time promise considerable improvement in DMFC membrane technology. This research, carried out in close collaboration with Virginia Polytechnic Institute, led to the demonstration of two new polymers from the poly (arylene ether sulfone) family: 6F and 6F-CN. Changes in the physicochemical properties of the non-fluorinated BPSH polymer brought about by the presence of $-CF_3$ (lower water uptake and better adhesion) helped to significantly reduce the interfacial

resistance between the membrane and the electrodes while preserving good selectivity. Consequently, the initial DMFC performance of the two new membranes was found to be better than that of Nafion[®] 117 under the same test conditions (Figure 3). Unlike non-fluorinated BPSH membranes, which suffer from irreversibly reduced performance after only 100 hours, 6F-CN-35 showed no degradation in the first 200 hours of life testing and only a slight performance drop after 700 hours. 6F-CN-35 exhibited no increase in high-frequency resistance over the time of the life test, suggesting a good and stable membrane/electrode interface. This result represents a significant achievement in alternative DMFC membrane research.

In parallel with the fundamental research in catalysis, membranes and MEAs, which has remained the focal point of the direct methanol fuel cell program at LANL, we also made substantial progress in the design and prototyping of DMFC stacks for portable and auxiliary power applications. Three generations of highly efficient and lightweight 11-W stacks were developed for the operation at a design voltage of 0.55/cell. Four units from the last generation were supplied to our system partner, Ball Aerospace & Technologies Corporation, for integration into two 20-W system prototypes for the military (a DARPA-sponsored project).

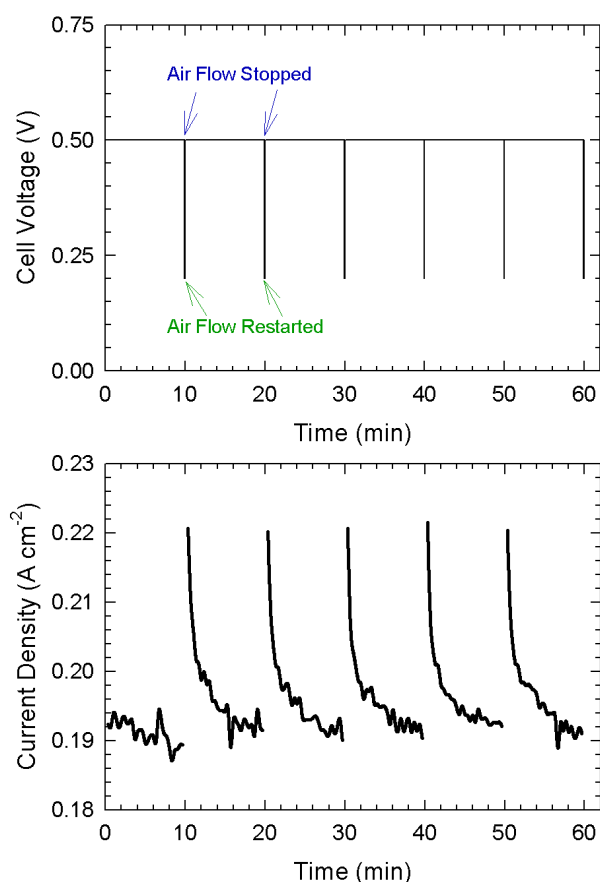


Figure 2. Effect of Cell Voltage (Cathode Potential) Pulsing on the DMFC Operation at 80°C

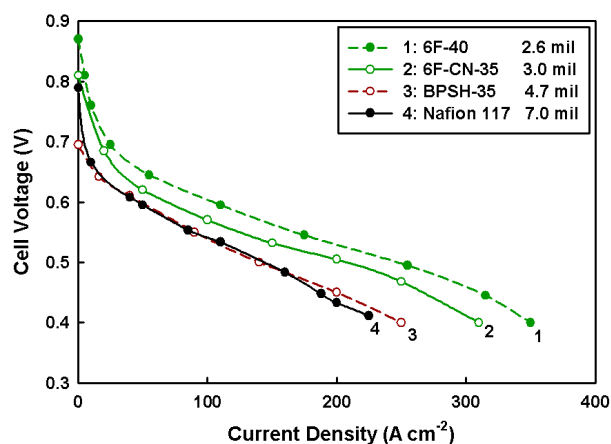


Figure 3. DMFC Polarization Plots Obtained with Four Different membranes: Nafion[®] 117, 6F-40, 6F-CN-35 and BPSH-35 (Plots recorded at 80°C and an ambient cathode air pressure of 0.76 atm in Los Alamos)

All key components for the 500-W APU stack were designed and tested in a six-cell stack, which preceded the construction of the actual stack deliverable scheduled in a few months. The short stack was assembled using 100-cm² active area cells. All six cells in the short stack exhibited uniform and good performance when operated at ambient cathode pressure and an air stoichiometry ratio of 3.0. The maximum power generated by the stack under these conditions was measured at 140 W (Figure 4), with negligible penalty on a scale-up from the single cell to the stack. As a result, the number of cells in the full stack required to generate the design power of 500 W is estimated at approximately 50, significantly lower than the originally planned 100.

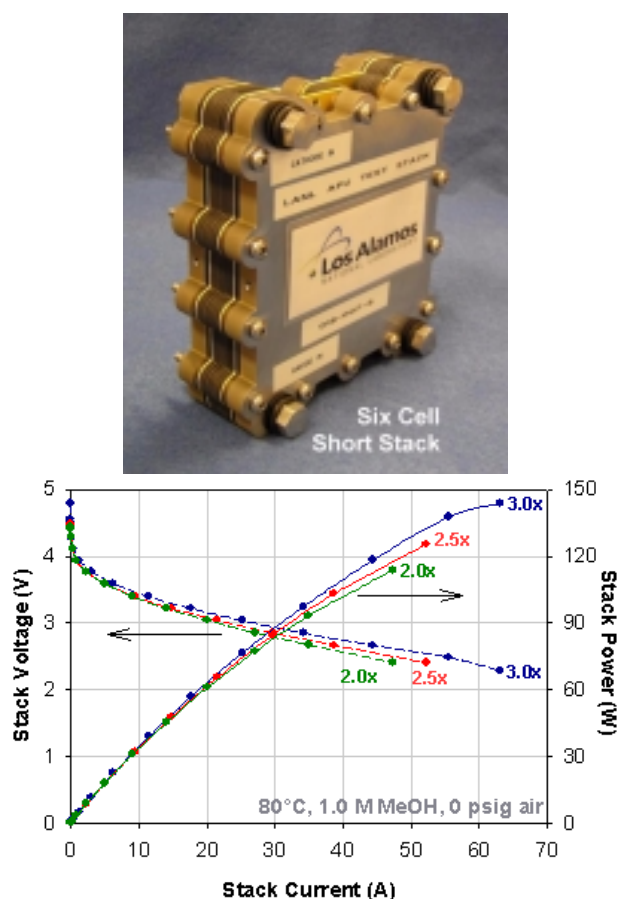


Figure 4. Development of 500-W DMFC Stack for Auxiliary Power System: Polarization and Power Plots for Six-Cell Stack at 80°C

Conclusions

The main conclusions from the DMFC research performed at LANL in the past year can be summarized as follows:

- The use of carbon-supported Pt catalyst with a Pt-to-C ratio of 50 - 60 wt% significantly reduces the catalyst loading at only a moderate performance penalty. Careful optimization of the cathode structure allows for continuous cell/stack operation at an air stoichiometric ratio as low as two.
- DMFC cell/stack suffers from short- and long-term performance loss. The short-term loss is predominantly caused by the oxidation of the cathode Pt. This loss can be reversed by intermittent reduction of the catalyst. Long-term performance degradation results from irreversible changes to the structure of the electrode and the hydrophobic/hydrophilic properties of the cathode, as well as from Ru crossover. Mitigating the long-term durability issues will require modifications to the MEA components and methods of cell fabrication.
- Thanks to low impedance of the membrane-electrode interface and preserved high selectivity, two new membranes from the BPSH family, 6F and 6F-CN, exhibit superior DMFC performance to Nafion[®] 117. Based on the life test data for 6F-CN-35, the membranes also promise good durability.
- Significant practical potential of DMFC technology was demonstrated with the 11-W stack prototypes operating at low flow and ambient pressure of the air. The stack power density, already measured at 130 W kg⁻¹, is expected to exceed 300 W kg⁻¹ soon, both for low power (11-W) and high power (500-W) stacks.

FY 2003 Publications

1. "Direct Methanol Fuel Cells: Progress in Cell Performance and Cathode Research," S. C. Thomas, X. Ren, S. Gottesfeld and P. Zelenay, *Electrochim. Acta*, 47, 3741-3748 (2002).

2. "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
3. "The Effect of BPSH Post Treatment on DMFC Performance and Properties," M. Hickner, Y. Kim, J. McGrath, P. Zelenay and B. Pivovar, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
4. "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation," Y. Zhu, E. Brosha and P. Zelenay, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
5. "Electrochemical and XRD Characterization of Pt-Ru Blacks for DMFC Anodes," C. Eickes, E. Brosha, F. Garzon, G. Purdy, P. Zelenay, T. Morita and D. Thompsett, in Proton Conducting Membrane Fuel Cells III, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
6. "Processing Induced Morphological Development in Hydrated Sulfonated Poly(arylene ether sulfone) Copolymer Membranes," Y. S. Kim, L. Dong, M. Hickner, B. Pivovar, and J. McGrath, Polymer, accepted for publication June 13, 2003.
2. Gordon Research Conference on Fuel Cells, Bristol, Rhode Island, July 28 - August 2, 2002. Title: "DMFC Research at Los Alamos: Towards Better Performing Cells and Stacks" P. Zelenay* (invited/keynote lecture).
3. 202nd Meeting of the Electrochemical Society, Salt Lake City, UT, October 20-24, 2002. Title: "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar*, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay.
4. 202nd Meeting of the Electrochemical Society, Salt Lake City, UT, October 20-24, 2002. Title: "The Role of Membrane Thickness and Interfaces on DMFC Properties," M. Hickner and B. Pivovar*.
5. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "The Effect of BPSH Post Treatment on DMFC Performance and Properties"; M. Hickner*, B.S. Pivovar, Y. Kim, J. McGrath and P. Zelenay.
6. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Modeling the Direct Methanol Fuel Cell Anode"; C. Diniz*, R. Moore, P. Badrinarayanan and P. Zelenay.
7. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Understanding the Cathode of A Direct Methanol Fuel Cell"; P. Badrinarayanan*, R. Moore, C. Diniz, J. Cunningham and P. Zelenay.
8. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation"; Y. Zhu*, E. Brosha and P. Zelenay.
9. 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 20-24, 2002. Title: "Electrochemical and XRD Characterization of Pt-Ru Blacks for DMFC Anodes"; C. Eickes*, E. Brosha, F. Garzon, G. Purdy, P. Zelenay, T. Morita and D. Thompsett.

FY 2003 Presentations

1. W. L. Gore, Elkton, Maryland, June 20, 2002. Title: "Direct Methanol Fuel Cells"; P. Zelenay* (invited lecture).

10. The International Battery Association and 5th Hawaii Battery Conference, Ernest B. Yeager Memorial Symposium, Waikoloa, Hawaii, January 7-10, 2003. Title: "Electrocatalysis in Direct Methanol Fuel Cells"; P. Zelenay (invited lecture).
11. Workshop on "Advances in Materials for Proton Exchange Membrane Fuel Cell Systems," Asilomar, California, February 23-27, 2003. Title: "Direct Methanol Fuel Cell Research at Los Alamos: From Fundamentals to Stacks"; P. Zelenay (plenary lecture).
12. Workshop on "Advances in Materials for Proton Exchange Membrane Fuel Cell Systems," Asilomar, California, February 23-26, 2003. Title: "The Influence of Polymer Structure on Fuel Cell Electrolyte Properties"; B. S. Pivovar (invited talk).
13. Columbia University, Department of Chemical Engineering, New York, NY, April 22, 2003. Title: "Effect of Polymer Structure on Fuel Cell Properties"; B. S. Pivovar (invited talk).
14. 203rd Meeting of the Electrochemical Society, Paris, France, April 27 - May 2, 2003. Title: "Methanol Crossover in Direct Methanol Fuel Cell Systems"; B. Pivovar*, G. Bender, P. Piela and P. Zelenay.
15. 203rd Meeting of the Electrochemical Society, Paris, France, April 27 - May 2, 2003. Title: "State of the DMFC Cathode During Prolonged Cell Operation"; C. Eickes, P. Piela and P. Zelenay*.
16. Seminar "Electrocatalysis in PEM Fuel Cells", Trondheim, Norway, May 5, 2003. Title: "Electrocatalysis in Direct Methanol Fuel Cells"; C. Eickes, P. Piela and P. Zelenay* (invited lecture).
17. Annex XI Meeting of International Energy Agency Meeting, May 6 - 7, 2003, Trondheim - Bergen, Norway. Title: "20 W DMFC System Development at LANL"; P. Zelenay*.